



Total ammonia nitrogen removal from aqueous solutions by the natural zeolite, mordenite: A laboratory test and experimental study



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ABSTRACT

The effectiveness of two processed samples of New Zealand mordenite for possible use in removing total ammonia nitrogen (TAN) in aquaculture application was studied. The percentage reduction in TAN concentration in 100-mL solutions held on a rotating shaker increased linearly with greater mordenite application rate, while the amount of TAN removed per gram of mordenite (adsorptive efficiency) declined. At a TAN concentration of 200 mg L⁻¹, both mordenite samples had an adsorption efficiency of about 8.7 mg TAN g⁻¹. Ammonia removal and adsorptive efficiency decreased with increasing salinity up to 30 g L⁻¹. In aquarium tests with less vigorous mixing, mordenite at concentrations equivalent to 10 to 500 kg ha⁻¹ in ponds removed only 1 to 8% of TAN from water. Mordenite and other zeolites are not useful for removing TAN from ponds. The New Zealand mordenite was of good quality and like other zeolites could be used for other applications in aquaculture such as small, intensively-stocked transport and holding units for aquatic animals, water recirculating culture systems, and possibly as a feed additive.

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1. Introduction

Zeolites are naturally occurring, synthetic minerals with a three-dimensional framework formed by silica–oxygen tetrahedrals in which some of the Si⁴⁺ has been replaced by Al³⁺ in the porous lattice-work resulting in a negative charge that imparts cation exchange properties to zeolite (Mumpton and Fishman, 1977). Zeolite filters are used for softening water for household use; sodium on zeolite is exchanged for calcium and magnesium in water. Zeolites are used in industry for cation exchange, molecular sieving, catalysis, and sorption processes (Jorgensen et al., 1976; Yusof et al., 2010). Zeolite also has been used to remove ammonia nitrogen from wastewater (Reeves, 1972; Yusof et al., 2010).

Mordenite, the zeolite studied here, is a common alteration product of pyroclastic sediment, sedimentary rock, and lava flows of worldwide distribution. It is an orthorhombic zeolite of high silica content (Deer et al., 2004). The ideal composition of mordenite is [(Na₂K₂Ca)₄Al₈Si₄₀O₉₆] 28H₂O. Mordenite contains 0.45% potassium, 2.29% calcium, and 2.89% sodium, while clinoptilolite, the zeolite commonly used in research on zeolite applications, is 3.21% potassium, 1.25% calcium, and 1.79% sodium (Passaglia, 1975; Simoncic and Armbruster, 2004).

Mordenite often is modified during processing to tailor its pore size and shape to meet the criteria for specific applications (Corma et al., 1994; Lin et al., 2013). It has been widely used as a catalyst in industrial

processes such as hydrocracking, hydroisomerization, alkylation and reforming (Bajpai, 1986; Shaikh et al., 1993), and for adsorptive separation for gas or liquid mixtures (Shao, 2002). Mordenite also is used as a host matrix in semiconductors, chemical sensors and selective membrane (Gilbert and Mosset, 1998).

The main interest in zeolites in aquaculture relates to control of total ammonia nitrogen (TAN) concentration. Ammonia is toxic to fish, shrimp, and other aquatic animals, and zeolite is used to lessen TAN concentrations in aquaria, fish holding tanks, water recirculating aquaculture systems, and containers of water for transporting aquatic animals (Bower and Turner, 1982; Boyd and Tucker, 1998; Johnson and Sieburth, 1974). Ammonia removal by zeolite is possible, because ammoniacal nitrogen exists as ammonium (NH₄⁺) and ammonia (NH₃) in a pH and temperature equilibrium as follows:



The proportion of ammonium decreases with increasing pH, but even at pH 9.0, ammonium comprises about 70% of the ammoniacal nitrogen in water (Trussell, 1972). Removal of ammonium by zeolite will lower the TAN concentration and thereby lessen the concentration of ammonia at equilibrium.

Shrimp farmers in Thailand and other Asian countries often apply zeolite to ponds at 180 to 350 kg ha⁻¹ in attempts to lower the concentration of ammonia to which culture animals are exposed, but there are no research findings to support this practice (Tonguthai, 2000). Moreover, zeolite products sold in Thailand (and presumably in other Southeast Asian countries) usually have a cation exchange

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capacity (CEC) less than 50 meq 100 g⁻¹ and do not absorb appreciable ammonium (Silapajarn et al., 2006). Chiayvareesajja and Boyd (1993) suggested that zeolite was not effective in removing TAN from pond waters – especially those filled with brackishwater and ocean water – because of competition for cation exchange sites on zeolite by other cations in water.

According to Yusuf et al. (2010), there have been many studies of natural zeolites – particularly clinoptilolite – for removing ammonium from wastewater. The results of these studies do not provide much useful information related to use of zeolites in aquaculture, because TAN concentrations in wastewater are much greater than in waters of aquaculture systems. A laboratory study was undertaken to ascertain if New Zealand mordenite has potential to lower TAN concentrations in waters of aquaculture systems.

2. Materials and methods

Two samples of mordenite were supplied by Blue Pacific Minerals, Tokora, New Zealand. Bulk density of the samples was determined by weighing 100-cm³ of each. Cation exchange capacity was obtained by the magnesium chloride technique (Rhoades, 1982) and by the neutral ammonium acetate method (Jackson, 1958; Kitsopoulos, 1999). Particle size was determined by passing known quantities of the two products through nested sieves of the following aperture sizes: 850, 425, 250, 150, 106, 75, 53, and 43 μm and weighing the amount of particles retained on each sieve. The pH was determined by glass electrode in 1:2 mixtures of mordenite:distilled water (Thunjai et al., 2001). Color was assessed with a Munsell color chart (Kollnorgen Instruments Corporation, New Windsor, New York).

Ammonium adsorption by the two mordenite samples was assessed under different conditions by adding weighted quantities to triplicate, 100-mL solutions containing known TAN concentrations. The following trials were conducted: (1) 1.00-g mordenite and TAN concentrations ranging from 0 to 200 mg L⁻¹ and prepared in distilled water; (2) mordenite amounts ranging from 0 to 100.0 g L⁻¹ in TAN concentration of 1 mg L⁻¹ prepared in distilled water; (3) 1.00-g mordenite and TAN concentration of 1.00 mg L⁻¹ in selected salinities between 0 and 30 g L⁻¹; and (4) 1.00-g mordenite in TAN concentration of 5.00 mg L⁻¹ in solutions also containing either sodium, potassium, calcium, or magnesium at selected concentrations between 0 and 50 meq L⁻¹.

In the trials, TAN concentrations were obtained from ammonium chloride (NH₄Cl). The different salinities were prepared by adding appropriate amounts of Instant Ocean® to distilled water. The different concentrations of major cations were made in distilled water using sodium chloride (NaCl), potassium chloride (KCl), magnesium sulfate (MgSO₄ · 5H₂O), and calcium nitrate [Ca(NO₃)₂]. The trials were conducted in a room where temperature varied from 22 to 26 °C. The flasks were agitated for 24 h on a mechanical shaker at 150 oscillations min⁻¹. The pH of solutions was measured with a glass electrode before shaking. After shaking, solutions were filtered (Whatman Number 42 paper) to remove mordenite particles and TAN concentrations in filtrates were measured by the salicylate technique (Bower and Holm-Hansen, 1980; Le and Boyd, 2012).

The capacity of mordenite to lower TAN concentration also was tested in 20-L aquaria filled with freshwater (0.1 g L⁻¹ salinity) and containing 3.0 mg L⁻¹ TAN from ammonium chloride. Mordenite was applied to each of four aquaria at 0, 1, 5, 20, and 50 mg L⁻¹; equivalent to approximately 10, 50, 200, and 500 kg ha⁻¹ in a 1-ha pond of 1 m average depth. Aeration was applied continuously via an air stone (5 cm long × 1.5 cm diameter) to gently mix the water in two aquaria at each mordenite concentration, but the other two aquaria were not aerated. Water samples were removed from each aquarium after 24 h for measurement of pH and TAN concentration.

3. Results

The two mordenite samples were yellowish in color, acidic, and of low bulk density (Table 1). Sample 1 was of much finer particle size than sample 2 (Fig. 1). Nearly 60% of particles in sample 1 passed a sieve with 250 μm apertures while only about 0.5% of particles in sample 2 were that small. The CEC values ranged from 93.3 to 119.8 meq 100 g⁻¹. The CEC was around 6% greater for sample 1 than for sample 2 by both CEC methods. However, the CEC measured by the ammonium acetate method was approximately 20 meq 100 g⁻¹ greater than the CEC determined by the magnesium chloride procedure for both samples. The ammonium acetate technique has been reported to give high results for acidic soil samples (Ross and Ketterings, 1995). Nevertheless, Kitsopoulos (1999) recommended using the ammonium acetate method for determining the CEC of mordenite. The manufacturer's website states that the New Zealand zeolites have a CEC typically greater than 100 meq 100 g⁻¹—this agrees fairly well with the CECs measured here.

Some studies have reported higher CECs for mordenite samples. For example, 80 mordenite samples from Santorini and Polyegos Islands of Greece (Kitsopoulos, 1999) had an average CEC of 130 meq 100 g⁻¹ (range = 1.70 to 200.4 meq 100 g⁻¹). Wang (2009) reported that mordenite had a CEC of 187 meq 100 g⁻¹, and a value of 164 meq 100 g⁻¹ was given by Sprynskyy et al. (2005). However, samples mentioned above had been pulverized to pass a sieve with 125 μm apertures. Particles of sample 1 that passed a screen with 250 μm apertures and particles that passed a screen with 53 μm apertures were analyzed for CEC; the results were 136 meq 100 g⁻¹ and 208 meq 100 g⁻¹. Thus, the lower CEC in the commercial products from New Zealand than in mordenite samples studied in previous research probably was related to particle size rather than to a natural property of the New Zealand mordenite.

The main reason for this investigation relates to zeolite use in aquaculture; therefore, the properties of the two mordenite samples were compared with properties of 25 different zeolite products purchased in shrimp farming supply stores in Thailand (Silapajarn et al., 2006). Only four of those samples were yellowish in color—the others were various shades of white and gray. The density of the samples from Thailand averaged 1.01 g cm⁻³ (range = 0.57 to 1.40 g cm⁻³), and the average pH was 6.98 (range = 4.11 to 12.03). Most of the zeolite samples from Thailand were finely pulverized—more than 50% of all but two samples passed a screen with 250 μm apertures. The CEC of the samples from Thailand tended to be quite low; the average was 34.4 meq 100 g⁻¹ (range = 2.7 to 147.8 meq 100 g⁻¹). Only four of 25 samples had CECs above 80 meq 100 g⁻¹. The two mordenite samples of the present investigation had a greater CEC than all but two of the Thailand samples.

The percentage reduction in TAN concentration from the solution and the quantity of TAN removed per gram of mordenite are presented in Fig. 2. In the 100-mL solutions with 1.00 g of mordenite, as the concentration of TAN in the water increased from 1 mg L⁻¹ to 200 mg L⁻¹, the removal percentage by mordenite decreased quickly, while the amount of TAN removed per gram increased drastically.

When TAN concentration was 200 mg L⁻¹, the adsorptive efficiency for these two mordenite samples was roughly 8.70 mg TAN g⁻¹ zeolite, while TAN removal percentage was about 43% for both mordenite samples. This result agrees well with those obtained by Marking and Bills

Table 1
Physical and chemical properties of two, New Zealand mordenite samples.

Variable	Sample 1	Sample 2
Color (Munsell color units)	8/6 (yellow)	8/4 (pale yellow)
Bulk density (g cm ⁻³)	0.606	0.727
Median particle diameter (μm)	200	660
pH cation exchange capacity (meq 100 g ⁻¹)	5.48	6.06
Magnesium chloride method	98.8	93.3
Neutral ammonium acetate method	119.8	112.0

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